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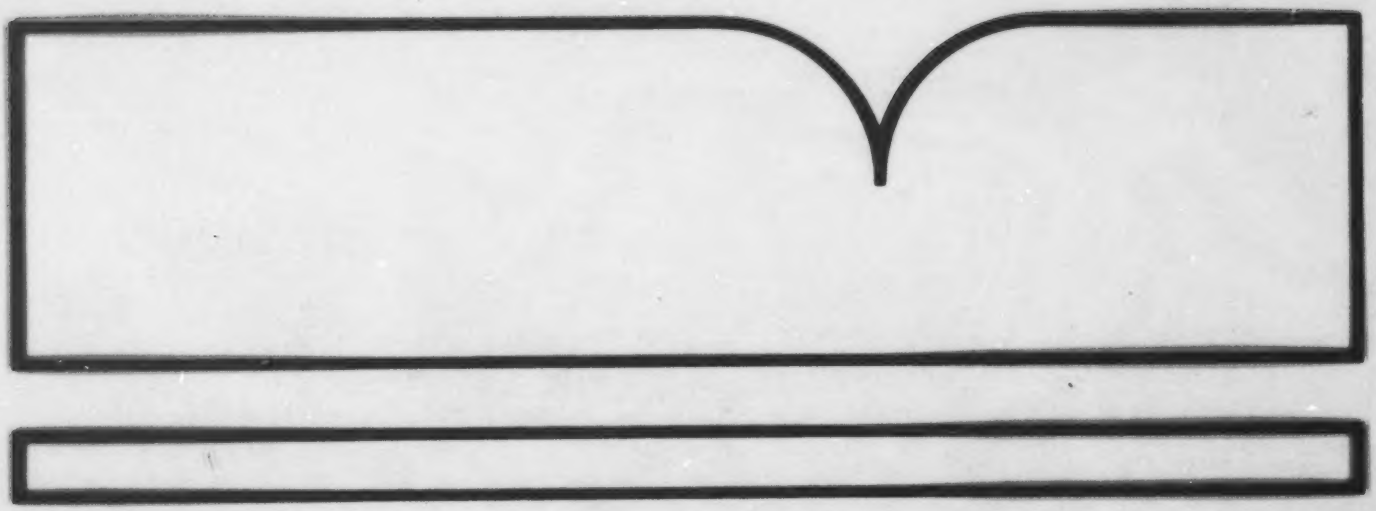

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16. ABSTRACT

Present acid forming emissions to the atmosphere have the potential to alter significantly the chemistry of rain, snow, and surface water of weakly buffered lakes in the Upper Midwest. Average precipitation pH from field measurements during 1979-1983 declined from west to east from 4.8, 4.6, and 4.3 along a cross-section of sites in Minnesota, Wisconsin, and Michigan respectively where 990 lake and stream sampling sites were studied. Measurements of weakly buffered lakes show a parallel decline in lake water pH with the lowest values measured, 5.1, 4.6 and 4.4, respectively in the same regions. Correspondingly, the percentage of lakes sampled with little or no acid neutralizing capacity (ANC) was found to increase from 0 to 4 and 13%, respectively. The geographic patterns in ionic composition of airborne acids and bases, and the resultant surface water concentrations are compared. The acid forming capacity (AFC) from airborne inputs is calculated using mass balance and in-lake processes. Stoichiometric acid-base reactions are used to balance the observed chemical differences between airborne inputs and surface water composition considering nitrification, denitrification, other oxidation-reduction reactions, and the evaporation concentration process. Microbial activity in surface water can result in a net decrease in ionic strength from the conversion of most of the ammonium and nitrate to neutral compounds and biomass, but only a partial reduction of about 20% of the sulfate inputs to weakly buffered lakes. The resulting AFC of airborne inputs are calculated to range from 30 to 60, 50 to 90, and 80 to 130 $\mu eq\ H^{+}L^{-1}$, respectively, in northeastern Minnesota-Ontario, northcentral Wisconsin and northern Michigan-Ontario. The differences in AFC of airborne inputs from west to east, and differences in in-lake processes explain the observed acidity of weakly buffered lakes across the region.

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IONIC COMPOSITION OF ACID LAKES IN RELATION TO AIRBORNE INPUTS AND WATERSHED CHARACTERISTICS

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80 to 130 μeq H^+L^{-1}, respectively, in northeastern Minnesota-Ontario, northcentral Wisconsin and northern Michigan-Ontario. The differences in AFC of airborne inputs from west to east, and differences in in-lake processes explain the observed acidity of weakly buffered lakes across the region.

1. INTRODUCTION

One of the major unresolved questions about the acidification of lakes continues to be whether observed lake chemistry is or is not primarily the result of chemicals from atmospheric inputs after watershed processing. Simple stoichiometric and mass balance modeling on a population of lakes could be used to evaluate the extent of correspondence between input chemistry and in-lake concentrations. This paper applies established principles of mass balance, evaporative concentration and biological processing of chemicals to determine whether precipitation inputs influence lake responses.

The compounds contributing most to the differences in precipitation chemistry across three Great Lakes States (GLS) of Minnesota, Wisconsin, and Michigan, offer the potential for understanding regional and local variation in pH, ionic compositions, acid-forming precursors, their reactive products (SO_4^{2-}, NO_3^-, H^+, and NH_4^+), and subsequent impacts on surface water quality (Glass and Loucks, 1986). Soil- and agriculturally-derived ions (Thornton and Eisenreich, 1982; Munger, 1982; Guiang et al., 1984) also need to be considered as inputs to surface water relating to geographic variations in rainfall chemistry (Glass and Loucks, 1980; Stensland and Semonin, 1982; Cogbill and Likens, 1982; Likens and Butler, 1981). The objectives of this paper are, therefore: to evaluate the significance of geographic patterns in the ion composition of acidic and basic reactants in precipitation and surface water across the GLS region and to compare the concentrations of acid and base forming compounds as atmospheric inputs with the resulting surface water chemistry.

2. METHODS*

The precipitation data reported in this analysis are summarized, in part, from a complete reporting and analyses by Glass and Loucks (1986). Sampling and analyses of 990 surface water sites in the study region began in the fall of 1978 in Minnesota, 1979 in Wisconsin, 1981 in Michigan and Ontario and continued through the summer of 1983 (see Table I). The water bodies were chosen using the sensitivity criteria developed by Glass and Loucks (1980) with an approximately equal number of sensitive and non-sensitive lakes across each region with a 5 to 10% sampling frequency of the total lake populations. In-situ measurements of water quality and water samples were collected at mid-lake at a

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Table I. General distribution of the 990 lake and stream sampling sites for assessment of surface water sensitivity in the Upper Midwest States and a summary of the number of lakes and streams, and the frequency distribution of these sites in five ANC (sensitivity) classes (Glass, 1984).

Region		Acid Neutralizaton Capacity Interval (μeqL^{-1}) <0	0-39	40-199	200-499	500+	Total Sites
Minnesota-Ontario	%	-	0.4	41	37	22	46
	Count	0	2	186	166	100	454
Wisconsin	%	4	23	23	24	28	45
	Count	20	100	99	105	121	445
Wisconsin[1] Total	%	1	6.8	30.6	61.6		100
Total	Count	142	967	4,369	8,783		14,261
Michigan-Ontario	%	13	10	19	17	42	9
	Count	12	9	17	15	38	91
Totals	%	3.2	11.2	30.5	28.9	26.2	100
	Count	32	111	302	286	259	990

[1]Total inventory of lakes was available for all of Wisconsin from the Wisconsin DNR (1984).

depth of 1 m during spring and fall turnovers when the lakes were well mixed and during summer and winter stratification as well. Detailed sampling procedures and analytical methods are given in Rapp et al. (1985).

The lake chemistry data have been subjected to quality assurance procedures for single parameter measurements and inter-parameter relationships to identify outliers and evaluate possible systematic errors in measurement or manipulation using charge balance (APHA, 1980), calculated pH-alkalinity (Stumm and Morgan, 1981), and comparison of measured vs calculated conductivity (Quint and Viallard, 1978). The precision and accuracy (based on standard additions and USEPA and NBS standard samples) of the measurements are, on average, within 5% of expected values. Calculated conductivity for 11 ions was usually within 5% of measured conductivity and variations outside of 15% were considered as outliers. The water chemical data are given as mean values averaged from all samples taken over the 5 yr period of study. The mean for pH values was determined by averaging H^+ concentrations.

Watershed and lake morphometric characterization, water renewal

times, and hydrologic evaporative concentration factors were determined using pre-existing surveys, USGS topographic maps and long-term data from water atlases (Geraghty et al., 1973). A detailed description of these methods and the statistical methods of analysis are found in Eilers et al. (1983) and Rapp et al. (1985, 1986). Precipitation chemistry and atmospheric inputs were determined for individual watersheds using linear interpolation between the precipitation monitoring sites. Evaporative concentration by watersheds was also calculated using the ratio of chloride concentrations in precipitation to those of lake water. Sulfate concentration ratios were computed similarly using the wet plus dry fall values. The lakes with the lowest acid neutralizing capacities (ANC ≤ 0) (lowest terrestrial inputs to lake water) were selected for detailed study in this analysis to identify and examine characteristics controlling lake water quality. They are identified in Table III with relevant descriptive data.

3. RESULTS AND DISCUSSION

Geographic Patterns in the Ionic Composition of Airborne Acid and Base Forming Substances: Since the potential for adverse effects to aquatic resources is controlled by the total dose of polluting substances (concentration(s) x rate of uptake x time; U.S. EPA, 1976), the average concentrations as well as volume weighted averages of atmospheric inputs (loadings) are of interest (Table II). The proton concentration results from numerous reactions between acid-forming precursors, ion exchange, and neutralization reactions that occur with the specific mix of gaseous and particulate materials washed out of the atmosphere during a given precipitation event. Average precipitation pH from field measurements made during 1979-1983 declines from 4.8 in northeastern Minnesota, to 4.6 in northcentral Wisconsin and to 4.3 in the Upper Peninsula of Michigan. The average concentrations are important in evaluating the maximum chemical potential for chemical and biological reactions while the volume-weighted values are important in determining loadings and mass balance calculations. The major anion concentrations are indicative of strong acid precursors in the atmosphere across the region and the site averages are given in Table II and plotted in Figure 1A. The major cations, in addition to H^+ in descending order of average concentration, are NH_4^+, Ca^{2+}, Mg^{2+}, K^+ and Na^+. The gradient in acidic reactants and products is consistent with the regional pattern of sulfur and nitrogen oxide emissions from sources in the region (Altshuller, 1980). The sum of $SO_4^{2-} + NO_3^-$ closely parallels the sum of $H^+ + NH_4^+$, also indicating the anthropogenic sources of strong atmospheric acidity (Brosset, 1980; Gorham et al., 1984; Calvert, 1984; NRC/NAS, 1983).

The ammonium (NH_4^+) ion is an important reaction product of acid aerosols with gaseous ammonia, $H_2SO_4(s) + 2NH_3(g) \longrightarrow (NH_4)_2SO_4(s)$ (Munger, 1982; Brosset, 1980). Ammonia neutralizes H^+ in precipitation, but the ammonium ion serves as a major contributor to the acidic inputs to surface water due to microbial activity (nitrification) that occurs in surface water: $NH_4^+ + 2O_2 \longrightarrow 2H^+ + NO_3^- + H_2O$ (Schnoor and

Table II. Average and volume-weighted ion concentrations in precipitation for the 3-4 year period from July 1979 through November 1983 at three NADP sites.

Location	No. Samples	Precipitation cm yr^{-1}	Average and/Volume Weighted Average Ion Concentration, μeqL^{-1}										
			H^+	NH_4^+	SO_4^{2-}	NO_3^-	Cl^-	Ca^{2+}	Mg^{2+}	K^+	Na^+	(+)	(-)
Fernberg Road, Minnesota	119	75	12 11	23 15	39 25	25 14	6.0 2.9	17.8 8.9	9.9 3.6	1.2 0.9	7.2 2.8	42.4	41.9
Trout Lake, Wisconsin	161	83	21 22	25 20	49 37	30 21	5.5 2.8	21.1 10.6	7.0 3.2	1.2 0.7	5.9 2.5	59.0	60.8
Douglas Lake, Michigan	180	71	42 39	30 19	67 51	40 28	5.7 3.4	22.4 11.8	8.1 4.1	1.4 0.8	6.7 4.0	78.7	82.4

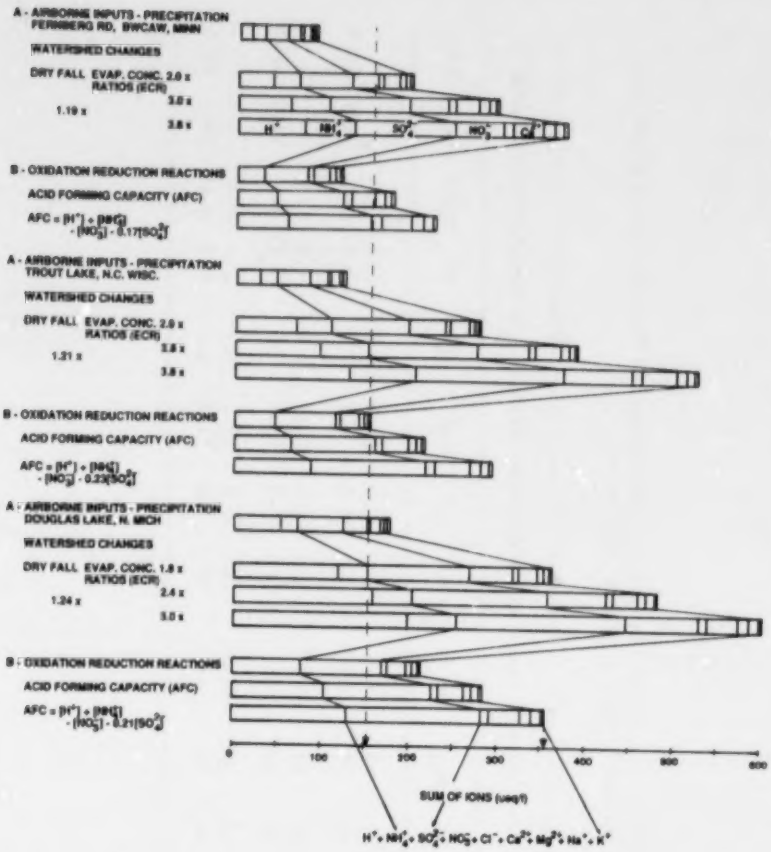

Fig. 1. Annual average ion concentrations in precipitation at monitoring sites showing the expected concentrations in unbuffered surface water following dry deposition and concentration by evaporation and redox reactions. Upper: the Boundary Waters Canoe Area Wilderness - Quetico Provincial Park regions of Minnesota and Ontario; Middle: the Nicolet and Ottawa National Forest regions of northcentral Wisconsin; and Lower: the Eastern Hiawatha National Forest - Pictured Rocks National Lakeshore region in Upper Michigan and near the Batchawana Mountain Lake Superior Provincial Park region of Ontario.

Stumm, 1984). In Table II, the ammonium and H^+ ions are the dominant cations, 67%. These, with the base cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+) are in ionic balance with sulfate, nitrate and chloride anions. The volume weighted average concentration of the sum of base cations is 19 $\pm$ 3 μeqL^{-1} for all sites (Table II) and results from ion exchange and acid neutralization reactions with H^+ and from the wash-out and weathering of soil particles (Verry, 1983).

Dry deposition of gases and particulates can increase the sulfate and nitrate deposition onto lakes and their watersheds by varying amounts depending upon many factors (Glass and Brydges, 1982). For the years 1981-1982, Chan et al. (1985) measured low level gaseous and particulate deposition and concluded that the dry components add an additional 19 to 24% SO_4^{2-} and 60 to 90% NO_3^- to the wet deposition values in northeastern Minnesota and northern Michigan, respectively. These values were used to estimate total acidic deposition to the study watersheds assuming that equivalent sulfate, nitrate, and H^+ are added.

Ion Composition and Potential Acid Forming Capacity (AFC) from Airborne Inputs to Surface Water: The changes from the chemistry of water as precipitation to that of surface water following input processes are complex and involve many physical, chemical and biological processes (Stumm et al., 1983; Glass and Brydges, 1982). For this study (focused on hydrologically isolated seepage lakes) we considered three major processes causing the changes in concentrations using a mass balance: evaporative concentration, nitrification-denitrification, and sulfate reduction.

Concentration of all ionic components in precipitation occurs by evaporative processes from water and from various terrestrial components within the watershed. The calculated results of predicted concentrations considering watershed evaporative concentration on atmospheric inputs (low, average and high values) are shown in Figure 1A together with the annual average (volume weighted) composition of precipitation in the three study regions.

Microbial and mediation reactions are known to occur for the more reactive components in precipitation that have nutrient properties (Schnoor and Stumm, 1984). These compounds can be modeled by stoichiometry of two oxidation-reduction reactions involving NH_4^+ and NO_3^-. The first is the nitrification process adding acidity:

$$NH_4^+ + 2O_2 = NO_3^- + H_2O + 2H^+$$ and the second is the denitrification process reducing acidity:

$$4NO_3^- + 5CH_2O + 4H^+ = 5CO_2 + 2N_2 + 7H_2O.$$

The complete reaction of one equivalent of each ion is assumed to result in no overall change in acidity or alkalinity content over long reaction times of several years, considering the water renewal times of the lakes (see Table III) (Schnoor and Stumm, 1984; Stumm et al., 1983; Schnoor et al., 1983). We modeled the reaction stoichiometry in precipitation in the short term and for correlation analyses to be $[H^+] + [NH_4^+] - [NO_3^-]$ since both NH_4^+ and NO_3^- reactions are essentially complete over the water renewal time of these seepage lakes, as indi-

Table III. Site, morphometric and watershed data for acidic lakes in the Upper Midwest study region.

Lake Name	County, State-Prov.	Lake Type (1)	pH	ANC μeqL^{-1}	Color Pt-Co	Evap. Conc. Ratio	Lake Area, ha	Depth Max. m	Water Renew. yr(2)
McNearney	Chippewa, MI	1	4.4	-38	3	2.2	50	7.5	41
Airhole	Langlade, WI	1	4.6	-26	115	2.7	34	3.0	25
Avery	Chippewa, MI	1	4.6	-27	45	1.9	6	3.0	11
Bear	Chippewa, MI	1	4.6	-24	54	2.2	36	3.6	7
Garlinghouse	Chippewa, MI	1	4.6	-27	7	3.4	17	3.7	20
Morgan	Florence, WI	1	4.6	-26	43	1.9	10	2.4	33
Denton	Vilas, WI	1	4.7	-12	110	2.6	10	10.1	28
Johnson	Chippewa, MI	1	4.8	-14	6	2.0	16	4.5	19
Stuart	Luce, MI	1	4.8	-17	6	2.2	30	6.9	25
Summit	Langlade, WI	4	4.8	-9	133	2.7	114	7.9	39
West Branch	Alger, MI	4	4.9	-14	70	2.1	15	2.7	12
Denton	Oneida, WI	1	4.9	-6	55	2.6	19	6.7	27
Malby	Oneida, WI	1	5.0	-7	6	2.7	18	4.0	16
Nineweb	Vilas, WI	1	5.0	-11	7	2.7	15	7.9	21
Bastille	Forest, WI	1	5.0	-12	10	2.5	18	7.0	40
Sand	Oneida, WI	1	5.0	-10	4	2.8	16	5.8	22
Silverbass	Oneida, WI	1	5.1	-8	5	2.7	11	3.4	20
Shallow	Oneida, WI	1	5.1	-4	9	2.7	11	2.1	16
Gordon	Vilas, WI	1	5.1	-7	10	3.1	21	5.5	23
McGrath	Oneida, WI	1	5.2	-5	7	3.3	20	7.3	21
Kelly	Luce, MI	1	5.2	-5	8	2.0	12	9.0	27
Clear	Langlade, WI	1	5.2	-1	9	3.1	35	7.0	42
Mill	Oneida, WI	1	5.2	-2	17	2.9	21	1.8	12
Long	Oneida, WI	5	5.2	1	10	1.8	8	2.0	8
JRO8	Algoma, Ont.	1	5.2	-5	7	2.9	43	9.4	34
Harmony	Vilas, WI	2	5.2	3	11	2.6	31	4.0	19
Camp 12	Vilas, WI	1	5.3	-0	6	2.7	34	8.2	26
JRO5	Algoma, Ont.	5	5.3	-2	30	1.8	8	3.0	10
Cusino	Schoolcft, MI	1	5.3	-1	22	2.1	53	10.8	19
Torch	Vilas, WI	1	5.3	0	7	2.7	16	4.3	17
Burrows	Oneida, WI	1	5.3	4	24	2.7	60	7.9	26
Deadmans	Luce, MI	1	5.4	-5	10	2.0	11	16.5	38
Sugar Camp	Oneida, WI	1	5.4	-0	4	3.8	210	11.6	32
Lumen	Oneida, WI	1	5.4	1	7	3.1	19	5.8	24
Great Bass	Oneida, WI	1	5.4	-1	15	3.0	45	4.6	17
Hildebrand	Lincoln, WI	1	5.4	1	7	2.8	23	7.3	34
Joyce	Vilas, WI	1	5.5	4	7	2.8	11	10.1	26
Scotchman	Oneida, WI	1	5.5	3	7	2.7	13	6.4	21
Luna	Forest, WI	1	5.5	5	5	3.0	26	4.8	25
Buteau	Lincoln, WI	1	5.6	2	6	3.2	21	15.2	46
Ike Walton	Vilas, WI	3	5.6	5	11	3.2	574	18.6	15

(1) Hydrologic type 1, seepage; 2, inflow; 3, drained; 4, drainage; 5, headwater; (Eilers, et al., 1983).
(2) Calculated from lake surface precipitation inputs.

cated by low lake water concentrations of these ions.

Sulfate reduction was measured using a simple mass balance comparison of present airborne inputs to lake water concentrations. Considering wet inputs alone, sulfate retention averages 77, 79, and 83% for the 20 most weakly buffered lakes in Wisconsin, Michigan, and Minnesota, respectively (see Figure 1). This difference was used to approximate the amount of sulfate reduction and associated H^+ consumption, and assumes lake sulfate to be in steady state with present inputs. The reduction reaction considered for sulfate is:

$$SO_4^{2-} + 2CH_2O + 2H^+ = 2CO_2 + H_2S + H_2O.$$

This reaction leads to an assumed upper limit on H^+ consumption since the lake data are really a time series and are dependent upon the watershed history preceding sample collection (Rapp et al., 1985).

Thus, the net result of oxidation-reduction reaction and mass balance stoichiometry gives the potential acid forming capacity for volume-weighted precipitation inputs:

$$[H^+], AFC = [H^+] + [NH_4^+] - [NO_3^-] - 0.2\,[SO_4^{2-}].$$

These results are shown graphically in Figure 1B where the expected maximum yields of H^+ are calculated considering the four processes described above. When all variations in evaporative concentration, wet and dry inputs, and oxidation-reduction reactions are calculated, total potential H^+ concentrations are calculated to be: 30 to 60, 50 to 90, and 80 to 130 μeqL^{-1}, respectively, for the resultant surface water across each state's (MN, WI, MI) study region on an annual basis. These results are shown in Figure 1B with the other ions resulting from airborne inputs as the resultant predicted concentrations for low, average and high evaporative concentration ratios (ECR). Lines connecting NH_4^+, SO_4^{2-} and K^+ are for comparative purposes for the range of watershed characteristics studied.

Additional reactions can occur, such as weathering, ion exchange, and synthesis/decomposition of biomass. These reactions can "consume" H^+ and produce increased concentrations of Ca^{2+}, Mg^{2+}, Na^+, K^+, Al(III), and SiO_2 (Schnoor and Stumm, 1984). The differences between predicted and measured lake composition can be seen by comparing Figure 1 with Figure 2 for 32 acid lakes in the study region.

Expected vs Observed Ionic Concentrations in Lake Water: The measured ionic concentrations of the most acid lakes listed in Table III are presented in bar-graph form in descending order of $[H^+]$ (Figure 2). The ionic concentrations in lake water are ordered along the bars to facilitate comparison with the concentrations for atmospheric inputs shown in Figure 1. Increased cations, Al, and organic anions generally account for the decreased H^+ that is expected considering atmospheric inputs. The broad pattern of surface water chemistry that corresponds with that of the precipitation chemistry can be seen in pH and ANC in surface water from 990 lake (861) and stream (129) sampling sites summarized in Table I. The lowest pH value from a lake in Minnesota was 5.1, in Wisconsin it was 4.6 and in Michigan it was 4.4. All of the

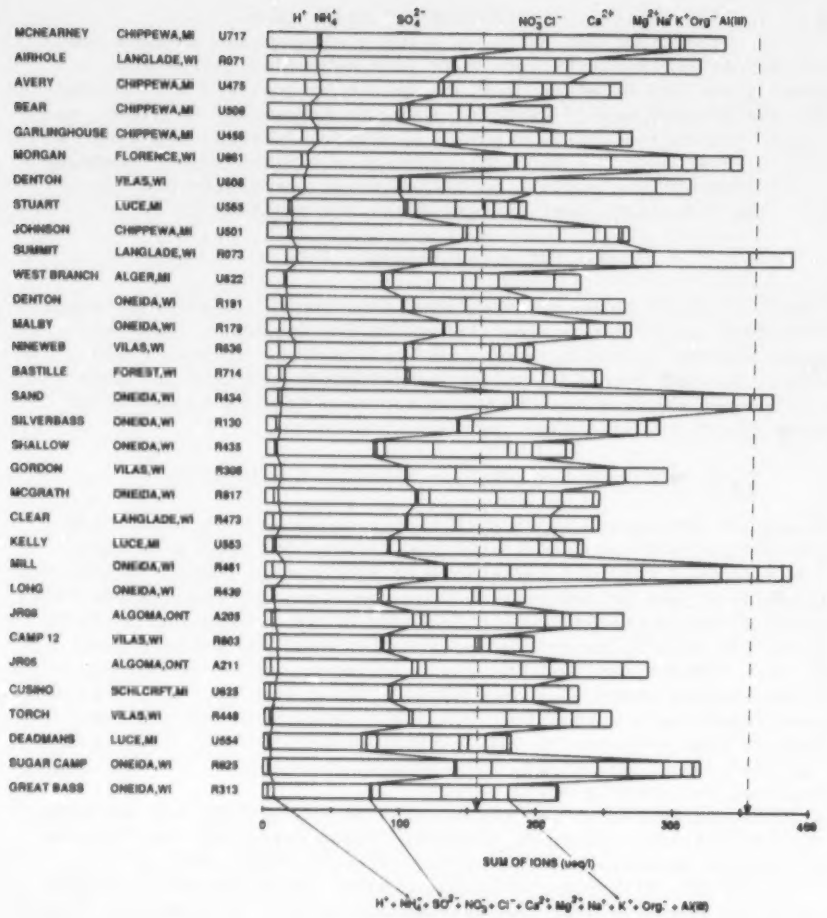

Fig. 2. Average ion concentrations for 32 acid lakes in the Upper Midwest study region. Dotted lines indicate the expected minimum and maximum resultant ion sums from atmospheric inputs and watershed factors given in Figure 1.

lakes in Minnesota/western Ontario showed positive measurable ANC, with all values greater than 40 μeqL^{-1}, except two. The 32 lakes showing strongest acidity (ANC <0) are found in Wisconsin and northern Michigan/central Ontario. This corresponds to 4% of the lakes in northcentral Wisconsin and 13% of the lakes in the eastern U.P. of Michigan.

Differences in lake water concentrations of ions from those predicted by atmospheric input can occur as a result of individual characteristics of the lakes, and processes induced in the lake basin by different reaction kinetics, ion exchange, dissolution of soil and sediment components, and cultural inputs (Glass and Brydges, 1982). The potential for these processes to yield varying concentrations of base cations, Al and corresponding bicarbonate, chloride and organic anions has been evaluated in a series of related studies (e.g., Rapp et al., 1985). Correlations obtained between watershed properties and strong acidity in these lakes show $[H^+]$ to be most strongly related to atmospheric acid forming inputs (indicating sources) and morphometric factors where weathering and ion exchange reactions are consuming H^+, Table IV. Conservative ion concentrations show positive correlations with evaporative concentration ratio and terrestrial anthropogenic influences, while the more reactive components, NH_4^+ and NO_3^- show negative correlations.

These results indicate that the most sensitive lake basins in the study region must annually supply a quantifiable amount of acid-neutralizing substances and/or ionic exchange substrate. This is to neutralize acid forming substances from atmospheric inputs due to differences in inputs and watershed characteristics in amounts of excess acid forming inputs ranging from 30 to 140 μeL^{-1} H^+, increasing from west to east across the region. Acidic waters and reduced resource value will result in basins that are unable to neutralize excess acidic inputs and maintain a lake pH above 6.5, the lowest pH value considered safe for an abundance of freshwater aquatic life (USEPA, 1976).

4. CONCLUSIONS

In a regional assessment of relationships between precipitation and surface water chemistry, care must be taken to consider a wide variety of potentially significant variables (Glass and Brydges, 1982; Rapp et al., 1985, 1986; Glass and Loucks, 1986). Physical and biological factors play key roles in the continuing dynamic changes in water chemistry as rock, soil, and sediment weathering contribute solutes; micro and macro organisms grow and cycle nutrients; and insoluble and particulate matter precipitate and accumulate as sediments in the basins. In this paper, local characteristics of precipitation and surface water composition have been considered in detail in relation to watershed processes transforming precipitation into surface water.

Two conclusions can be drawn that are relevant to the aquatic resources at risk from acidic deposition in northern Michigan, Wisconsin, and Minnesota. First, ions ($H^+ + NH_4^+$) from acid-forming gases (SO_x and NO_x) are observed in deposition with the resultant oxi-

Table IV. Selected correlation coefficients for lake water chemistry and selected atmospheric inputs and watershed variables for 41 acidic lakes.

Variable	Lake pH	Lake ANC	Lake Color	Lake Dep. Max.	L.Wat. Ren. Time	Evap. Conc. Ratio	Coni. For. %	N. Lat.	W. Long.	Prec. Depth	SO_4^{-2} Conc. Prec.	AFC
Lake ANC	+0.94 **											
Lake Color	-0.50 **	-0.34 *										
Lake Depth, Max.	+0.44 **	+0.33 *	-									
Lake Water Ren. Time	-	-	-	+0.51 **								
Evap. Conc. Ratio	+0.40 **	+0.36 *	-	+0.27	-							
Coniferous Forest, %	-0.31 *	-0.28	+0.44 **	-	-	-						
N. Latitude	-	-	-	-	-0.46 **	-0.75 **	-					
W. Longitude	+0.43 **	+0.48 **	-	-	-	+0.83 **	-0.26	-0.86 **				
Precip. Depth	+0.45 **	+0.47 **	-	+0.29	-	-	-	-	+0.44 **			
SO_4^{-2} Conc. in Precip.	-0.49 **	-0.54 **	-	-	-	-0.79 **	-	+0.72 **	-0.98 **	-0.57 **		
AFC; wet $[H^+] + [NH_4^+]$	-0.51 **	-0.56 **	-	-	-	-0.76 **	-	+0.65 **	-0.95 **	-0.62 **	+1.00 **	
AFC - total, wet & dry $[H^+] + [NH_4^+] - [NO_3^-] - 0.2\ [SO_4^{-2}]$	-0.51 **	-0.57 **	-	-	-	-0.75 **	-	+0.84 **	-1.00 **	-0.46 **	+0.98 **	+0.96 **

**significance <0.01; *significance <0.05 and ≥0.1; no designation <0.10 and ≥0.05

dation products (SO_4^{2-} and NO_3^-) ranging in potential concentrations (volume weighted) in surface water from 110 to 190 μeqL^{-1} and 50 to 80 μeqL^{-1}, respectively, from west to east across the region. After considering stoichiometric oxidation reduction reactions of NH_4^+, NO_3^-, and SO_4^{2-}, and evaporative concentration, the calculated AFC of acidifying substances in $\mu eq\ H^+\ L^{-1}$ of lake inflow water can range from 30 to 60, 50 to 90, and 80 to 130, respectively, in the study watersheds of Minnesota, Wisconsin and Michigan. The pattern in AFC must be considered with $[NH_4^+]$, $[NO_3^-]$, and $[SO_4^{2-}]$ in assessing anthropogenic acid-precursor sources and implications for acidification of hydrologically isolated surface waters such as seepage lakes.

Second, present-day atmospheric inputs of acid forming compounds show strong relationships with acidity of lakes (after considering watershed factors) in northern Michigan/Ontario (12 acid lakes, 13% of the sampling sites) and northcentral Wisconsin (20 acid lakes, 4% of the sampling sites). Inputs of AFC to these lakes appear to have exceeded the ability of the watersheds to neutralize precipitation inputs and the resulting lake water remains acidic. These mass balance calculations show that acidic atmospheric inputs can dominate lake chemistry, forcing close chemical correspondence between precipitaton inputs and acidic surface water composition. For the acid lakes studied in this analysis, the variations in the resultant lake water H^+ concentration were most strongly related to acid forming inputs and in-lake processes. Additional studies of similarities and differences in the receiving lake basins are required to determine whether the present atmopheric inputs are in equilibrium with the observed surface water chemistry or whether these inputs have induced changes in the aquatic and terrestrial resources of these regions.

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